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[54] Title of the Invention: A fluidized bed catalyst for acrylonitrile production

[57] Abstract

This invention is a type of fluidizing bed catalyst for acrylonitrile product characterized by the fact that the carrier silicon dioxide of the catalyst is a raw material preparation in which silicon sol is the raw material, and the average diameter of the colloidal particles of this silicon sol at the time of preparation is 10-200 nm, its concentration is 5-60% (weight percent), the sodium content in the silicon sol is 100-2500 ppm, and the pH of the silicon sol is 7-12. A catalyst prepared with the said carrier has the following advantages: a high degree of anti-abrasion strength, good catalytic activity, a simple preparation process, and easy control, so that catalytic activity is more suitable to the requirements of fluidized beds.

(BJ) Number 1456

## Claims

We claim:

1. A type of fluidized bed catalyst for use in the ammoxidation of propylene to manufacture acrylonitrile and that comprises a silicon dioxide carrier and mixture with the following chemical formula:



In the formula, A is potassium, rubidium, cesium, samarium, thallium, or a mixture of these; B is manganese, magnesium, strontium, calcium, barium, lanthanum, rare earth elements or a mixture of these; C is phosphorus, arsenic, boron, antimony, chromium, or a mixture of these; and M is tungsten, vanadium, or a mixture of these.

a is 0.01-1, b is 0.1-3, c is 0.01-2, d is 0.01-8, e is 0.01-12, f is 0.02-0.7, g is 0.01-8, h is 0.01-6, i is 0.01-6, j is 6-11.99, and x is a total atomic number that satisfies the chemical valence of each element in the catalyst; the combination of i and j in the formula always equals 12.

The amount of silicon dioxide carrier in the catalyst is 30-70% (weight percent). The optimal silicon sol is raw material in which the silicon sol concentration is confirmed to be 5-60% (weight percent). The diameter of the colloidal particles in the silicon sol is 10-200 nm; the pH, 7-12; and the sodium content in the silicon sol, 100-2500 ppm.

2. The catalyst described in Claim 1 characterized by the fact that the silicon sol concentration is 30-40% (weight percent).

3. The catalyst described in Claim 1 characterized by the fact that the diameter of the colloidal particles in the silicon sol is 15-90 nm.

4. The catalyst described in Claim 1 characterized by the fact that the pH of the silicon sol is 9-11.

5. The catalyst described in Claim 1 characterized by the fact that the sodium content in the silicon sol is 500-1500 ppm.

## Specifications

This invention relates to a fluidized bed catalyst for the propylene ammoxidation production of acrylonitrile and is characterized by a silicon dioxide carrier of the catalyst.

Acrylonitrile is an important organic raw material in the chemical industry and is produced by propylene going through an ammoxidation reaction. A great deal of research has been done to obtain a highly reactive fluidized bed catalyst with high selectivity and a series of advances have been made. For the most part, these advances have been related to catalyst activity component and very little has been done on catalyst carriers. In the process of propylene ammoxidation manufacture of acrylonitrile, it is generally possible to use catalyst carriers such as the following: silicon dioxide, diatomaceous earth, pumice, and quartz sand. However, silicon dioxide is used most often. The source of silicon dioxide in a catalyst can be silicon sol or silicon gel that is previously made into tiny balls of silicon sol or ethyl ester silicate, etc., with silicon sol being optimal.

While the silicon dioxide carrier has no catalytic activity in regard to the propylene ammoxidation production of acrylonitrile, it does have a major effect on dispersal conditions of the above-mentioned active component in the catalyst and on the porous structure and material properties of the catalyst. For fluid bed acrylonitrile catalysts, certain physical properties and anti-abrasion strength are extremely important.

Only a small amount of literature exists on advances in silicon dioxide carriers. Most of the published patents target antimony-system catalysts in which antimony oxide is used as the base component. For example, [Japanese] Examined Patent Application Sho 57-26592 proposes the following requirements in an antimony-system catalyst: average colloidal particle diameter in the silicon sol of 5-100 nm and silicon dioxide concentration of 10-60%. [Japanese] Examined Patent Application Hei 2-47264 proposes using two types of silicon sol with different colloidal particle diameters when manufacturing an antimony-system catalyst. The catalyst thus manufactured has comparatively good anti-abrasion strength. Colloidal particle diameter in the A type silicon sol is  $5 < D_a < 50 \text{ n}$ , and the B type colloidal particle diameter is  $0.1 < D_a/D_b < 0.9$ . There is even less literature on molybdenum-system catalysts. [Japanese] Examined Patent Application Hei 3-16177 proposes a silicon dioxide carrier that uses two components with manufacturing an antimonite catalyst: one type of microparticle silicon dioxide that is roasting manufactured with silicon tetrachloride at high temperature and another type that is a silicon sol. At the same time, these methods have been applied to the manufacture of molybdenum-system catalysts (US 4280929) to increase anti-abrasion strength. Of the above publications, the methods using silicon gel are very complicated, difficult to control, and require at least secondary additions of silicon sol. To obtain a type of more convenient catalyst preparation and, at the same time, to manufacture a catalyst with better strength and activity that is even better suited to propylene ammoxidation production of acrylonitrile fluidized beds, we discovered an even better type of catalyst.

The design of this invention is realized through the working examples described below. The fluidized bed catalyst used in this invention is composed of a mixture of a silicon dioxide carrier and the components of the following chemical formula:



In the formula, A is potassium, rubidium, cesium, samarium, thallium, or a mixture of these; B is manganese, magnesium, strontium, calcium, barium, lanthanum, rare earth elements or a mixture of these; C is phosphorus, arsenic, boron, antimony, chromium, or a mixture of these; and M is tungsten, vanadium, or a mixture of these.

a is 0.01-1, b is 0.1-3, c is 0.01-2, d is 0.01-8, e is 0.01-12, f is 0.02-0.7, g is 0.01-8, h is 0.01-6, i is 0.01-6, j is 6-11.99; the combination of i and j in the formula always equals 12; and x is a total atomic number that satisfies the chemical valence of each element in the catalyst.

The amount of silicon dioxide carrier in the catalyst is 30-70% (weight percent) and preferably 40-60% (weight percent).

The present inventors have disclosed improvement results of aspects such as chemical components, manufacturing methods, and industrial applications of related catalysts in Chinese Patents 1033014A (CN 1005248B), 1022439A (CN 1013079B), 1061163A (US 5177048), 1054914A (CN 1021638B, US 5223469, EP 484792A) and 1061166A, respectively. The present patent describes novel results of a silicon dioxide carrier related to the above catalysts.

The raw materials used in the catalyst of this invention were

component A that is preferably salt nitrate, hydroxide, or salts that decompose as an oxide;

component B, which can be an oxide or salts that can decompose as an oxide.

Component B is phosphorus and arsenic and boron that optimally use the corresponding acid or its ammonium salt, chromium that optimally uses chromium trioxide (six valence chromium) and chromium nitrate or a mixture of the two, antimony for which diantimony trioxide, diantimony pentoxide, halogenate of hydrolysable oxides and antimony sol can be used.

The following can be used for the component sodium: sodium nitrate, sodium hydrochloride, sodium silicate, or a decomposed sodium compound. The amount of sodium in the silicon sol should be deducted from the amount of added sodium.

The tungsten in component M can be in the form of tungsten oxide or ammonium tungstate. Metaammonium vanadate is used for the vanadium.

To ensure that the catalyst has a comparatively high level of activity and good anti-abrasion strength, a raw material made into a silicon dioxide carrier needs to use a type of specially stipulated silicon sol relative to the above-mentioned molybdenum-system catalysts. If the average colloidal particle diameter of the said silicon sol is too small, the pore size of the manufactured catalyst will be small, thus resulting in carbon overproduction of oxides at the time of ammoxidation and reduced selectivity. In addition, overly small colloidal particle size will cause the sprayed thick liquid to be excessively viscous and unstable, so that it is prone to gelling. If the colloidal particle diameter is too large, the manufactured catalyst will have poor anti-abrasion strength. The required average colloidal particle diameter of this patent is 10-200 nm and optimally 15-90 nm. The concentration of silicon dioxide in the silicon sol is 5-60% (weight percent), and optimally 30-40% (weight percent). If the concentration of silicon dioxide is too low, the manufactured catalyst will have a low degree of packaged density, resulting in high consumption. The pH value of the silicon sol and the chemical composition of the catalyst are related. The chemical formula described above in this patent supposes a pH value of 7-12 and

optimally 9-11. The sodium content in the silicon sol is 100-2500 ppm and preferably 500-1500 ppm.

The said silicon sol and catalyst components are mixed with water to form a paste, spray-dried and formed into micro balls, and finally put through roasting manufacture to create a catalyst. Paste preparation is done with an aqueous solution of the various catalyst components and the silicon sol according to the method described in Chinese Patent CN 1005248.

Use of a catalyst prepared according to the method described above results in good activity, selectivity, and anti-abrasion strength in a fluidized bed reactor and obtains the expected results.

Below are working examples of the catalyst of this invention. In them, the propylene conversion rate, acrylonitrile selectivity, and yield per pass are defined as follows:

propylene conversion rate (%) = (reacted propylene mole number) / (propylene added material mole number) X 100

acrylonitrile selectivity (%) = (produced acrylonitrile mole number) / reaction propylene mole number) X 100

acrylonitrile yield per pass (%) = (produced acrylonitrile mole number) / (propylene added material mole number) X 100.

#### Working Example 1

The following were mixed to form material (A): 9.2 g weight concentration 20% arsenic nitrate solution; 13.4 g weight concentration 20% rubidium nitrate, and 8.9 g weight concentration 20% cesium.

A total of 23.7 g ammonium tungstate was dissolved in 100 mL weight concentration 5% ammonium water and then mixed with 368.3 g ammonium molybdenate and 300 mL water heated to 50-95°C to form material (B).

A total of 79.2 g bismuth nitrate, 52.1 manganese nitrate, 131.9 g iron nitrate, 211.1 g cobalt nitrate, 121.3 g nickel nitrate, and 29.0 g chromium nitrate was mixed and added to 70 mL water, heated, and dissolved to form material (C).

The average colloidal particle diameter of the silicon sol to be used was 25 nm, the sodium content (calculated as sodium oxide) was 1350 ppm, and the pH was 9.

Material (A) and 1250 g weight amount, 40% concentration of the above-mentioned sodium solution were mixed, 5.23 g weight concentration 85% phosphoric acid and materials (B) and (C) added under agitation, and the solution adequately agitated to obtain a gel. According to the usual method, the gel was formed into micro balls during spray drying and finally roasted for 1 hour in a roasting furnace with an interior diameter of 89 mm and a length of 1700 mm.

The specific surface area of the manufactured catalyst was 25 m<sup>2</sup>/g. The packaged density was 0.98 g/mL, and the anti-abrasion strength was 2.7% (based on the *Test Methods for Synthetic Cracking Catalysts* measurement method).

The manufactured catalyst was placed in a fluidized bed reactor with an interior diameter of 38 mm. Results of the activity evaluation at a reaction temperature of 435°C, reaction pressure of 0.08 MPa, propylene : ammonium : air = 1:1:10.0 (moles), and [illegible] of 0.045.

propylene conversion rate:	97.5%
acrylonitrile yield per pass:	81.0%
acrylonitrile selectivity:	83.1%

#### Working Example 2

The amount of raw materials added was the same as in Working Example 1. The carrier silicon sol specifications were the same except for a sodium amount of 900 ppm, and the catalyst manufactured according to the method in Working Example 1 had a specific surface area of 16 m<sup>2</sup>/g and anti-abrasion strength of 4.0%. The activity evaluation conditions were the same as in Working Example 1. The results were as follows:

propylene conversion rate:	98.3%
acrylonitrile yield per pass:	81.5%
acrylonitrile selectivity:	82.9%

#### Working Example 3

The amount of raw materials added was the same as in Working Example 1. The carrier silicon sol specifications were the same except for a sodium amount of 500 ppm, and the catalyst manufactured according to the method in Working Example 1 had a specific surface area of 19 m<sup>2</sup>/g and anti-abrasion strength of 6.5%. The activity evaluation conditions were the same as in Working Example 1. The results were as follows:

propylene conversion rate:	99.4%
acrylonitrile yield per pass:	81.6%
acrylonitrile selectivity:	82.1%

As can be seen from this example, when the sodium content in the silicon sol is too low, the catalyst lacks anti-abrasion strength. Although the catalytic activity was comparatively high, acrylonitrile selectivity fell.

#### Working Example 4

A catalyst manufactured according to the method described in Working Example 1 was prepared by mixing the following ingredients:

material (A) made up of 9.0 g 20% weight concentration of cerium nitrate solution, 41.0 g samarium nitrate solution, and 24.6 g thalious nitrate solution;

material (B) made up of 24.1 g ammonium tungstate dissolved in 100 mL 5% weight concentration ammonium water solution, then mixed with 374.1 g ammonium molybdenate and 300 mL water heated to 50-95°C;

material (C) made up of 80.4 g bismuth nitrate, 134.0 g iron nitrate, 52.9 g manganese, 94.5 g magnesium nitrate, 107.2 cobalt nitrate, 123.2 nickel nitrate, 29.5 g chromium nitrate, and 70 mL water.

The sodium content in the carrier silicon sol was 1000 ppm, the average diameter of colloidal particles was 30 nm, the silicon dioxide content was 40% (weight per cent), and the pH was 9.5

The above-mentioned materials (A), (B), and (C) were mixed with 1250 g silicon sol and 5.3 g, 85% weight concentration phosphoric acid, spray molded, roasted, and formed into a catalyst.

The specific surface area of the manufactured catalyst was 16 m<sup>2</sup>/g, the packaged density was 1.02 g/mL, and the anti-abrasion strength was 3.0%. The activity evaluation conditions were the same as in Working Example 1. The results were as follows:

propylene conversion rate:	97.5%
acrylonitrile yield per pass:	79.5%
acrylonitrile selectivity:	81.5%

#### Working Example 5

A catalyst manufactured according to the method described in Working Example 1 was prepared by mixing the following ingredients:

material (A) made up of 11.0 g 20% weight concentration sodium nitrate, 17.5 g arsenic nitrate, and 8.5 g cesium nitrate;

material (B) made up of 4.1 g metaammonium vanadate and 361.0 g ammonium molybdenate mixed with 300 mL water heated to 50-95°C;

material (C) made up of 84.1 g bismuth nitrate, 140.0 g iron nitrate, 75.2 g cerous nitrate, 242.0 g cobalt nitrate, 74.6 g manganese nitrate, 18.7 g nickel nitrate, 11.5 g thallium nitrate, and 100 mL water.

The carrier silicon sol had a sodium content of 700 ppm, average colloidal particle diameter of 20 nm, weight concentration of 40%, and pH of 9.0.

The above-mentioned materials (A), (B), and (C) were mixed with 1250 g silicon sol and 16.1 g boric acid mixture, spray formed, and roasted for 0.5 hours at 600°C to manufacture a catalyst.

The specific surface area of the manufactured catalyst was 20 m<sup>2</sup>/g, the packaged density was 0.98 g/mL, and the anti-abrasion strength was 3.0%. The activity evaluation conditions were the same as in Working Example 1. The results were as follows:

propylene conversion rate:	98.0%
acrylonitrile yield per pass:	81.3%

acrylonitrile selectivity: 82.9%

#### Working Example 6

A catalyst was manufactured according to the method used in Working Example 5 with the amounts of the added components unchanged. The carrier silicon sol had a colloidal particle diameter of 5 nm, concentration of 25% (weight percent), pH of 8, and other specifications the same as in Working Example 5. When a catalyst was manufactured according to the method in Working Example 5, it was found that the viscosity was comparatively high, that spray forming was comparatively difficult, and that catalyst loss was comparatively large.

The specific surface area of the manufactured catalyst was  $21 \text{ m}^2/\text{g}$ , the packaged density was  $0.85 \text{ g/mL}$ , and the anti-abrasion strength was 3.8%. The activity evaluation conditions were the same as in Working Example 1. The results were as follows:

propylene conversion rate:	98.0%
acrylonitrile yield per pass:	80.6%
acrylonitrile selectivity:	82.2%

From this working example it can be seen that when the colloidal particles of the silicon sol are too small, there is a major effect on the physical properties of the catalyst, but the effect on catalytic activity is not large. Excessively low catalyst packaged density affects normal operation of the fluidized bed reactor and also makes manufacture of the catalyst difficult.

#### Working Example 7

A catalyst was manufactured according to the method used in Working Example 5 with the amounts of the added components unchanged. The carrier silicon sol had a colloidal particle diameter of 200 nm; other specifications were the same as in Working Example 5.

The specific surface area of the manufactured catalyst was  $23 \text{ m}^2/\text{g}$ , the packaged density was  $7.0 \text{ g/mL}$ , and the anti-abrasion strength was 3.8%. The activity evaluation conditions were the same as in Working Example 1. The results were as follows:

propylene conversion rate:	98.3%
acrylonitrile yield per pass:	79.8%
acrylonitrile selectivity:	81.2%

From this working example it can be seen that when the colloidal particles of the silicon sol are too large, the catalyst has poor anti-abrasion properties and is not suitable for use in a fluidized bed reactor.

#### Working Example 8

A catalyst was manufactured according to the method used in Working Example 4 with the amounts of the added components unchanged from those in Working Example 4. The carrier

silicon sol had a colloidal particle diameter of 80 nm; other specifications were the same as in Working Example 4.

The specific surface area of the manufactured catalyst was 28 m<sup>2</sup>/g. The activity evaluation conditions were the same as in Working Example 1. The results were as follows:

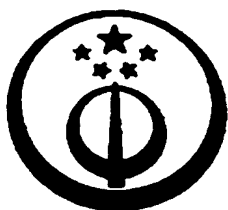
propylene conversion rate:	99.0%
acrylonitrile yield per pass:	76.4%
acrylonitrile selectivity:	77.2%

From this working example it can be seen that, although the diameter of the colloidal particles is within the stipulated range, the specific surface area is too large so that acrylonitrile selectivity drops, and a comparatively large amount of carbon dioxide is produced during the reaction.

If the roasting temperature of the catalyst of this working example is increased to 750°C and the roasting temperature changed to 45 minutes, the specific surface area of the manufactured catalyst is 22 m<sup>2</sup>/g. With activity evaluation conditions the same as in Working Example 1, the results were as follows:

propylene conversion rate:	97.6%
acrylonitrile yield per pass:	80.5%
acrylonitrile selectivity:	82.5%

This working example demonstrated that even though the particle diameters of the silicon sol were within the stipulated range, the diameters were not the same and that it is also necessary to adjust the roasting conditions to obtain the optimal results.



## [12] 发明专利申请公开说明书

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权利要求书 1 页 说明书 9 页 附图页数 0 页

[54]发明名称 生产丙烯腈的流化床催化剂

[57]摘要

一种用于生产丙烯腈的流化床催化剂,其特征在于催化剂的载体二氧化硅是以硅溶胶为原料制得的,制备时其硅溶胶的胶粒平均直径为 10~200 毫微米、浓度为 5~60% (重量),硅溶胶中的钠含量为 100~2500ppm,硅溶胶的 pH 值为 7~12。使用该载体制成的催化剂具有耐磨强度高,催化活性好,制备操作步骤简单、易于控制等优点,使该催化剂更适合流化床的要求。

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(BJ)第 1456 号

1. 一种用于丙烯氨氧化反应制取丙烯腈的流化床催化剂, 由二氧化硅载体和化学式如下的组合物组成:



式中A为钾、铷、铯、钐、铊或它们的混合物; B为锰、镁、锶、钙、钡、镧、稀土元素或它们的混合物; C为磷、砷、硼、锑、铬或它们的混合物; M为钨、钼或它们的混合物。

a为0.01~1, b为0.1~3, c为0.01~2, d为0.01~8, e为0.01~12, f为0.2~0.7, g为0.01~8, h为0.01~6, i为0.01~6, j为6~11.99, x为满足催化剂中各元素化合价所需的氧原子总数, 化学式中i与j的和恒为12。

催化剂中载体二氧化硅含量为30~70%(重量), 最好用硅溶胶为原料, 其特征在于硅溶胶的浓度为5~60%(重量), 硅溶胶的胶粒直径为10~200毫微米, 硅溶胶的PH值为7~12, 硅溶胶中钠的含量为100~2500ppm。

2. 根据权利要求1所述的催化剂, 其特征在于硅溶胶的浓度为30~40%(重量)。

3. 根据权利要求1所述的催化剂, 其特征在于硅溶胶的胶粒直径为15~90毫微米。

4. 根据权利要求1所述的催化剂, 其特征在于硅溶胶的PH值为9~11。

5. 根据权利要求1所述的催化剂, 其特征在于硅溶胶中钠含量为500~1500ppm。

## 生产丙烯腈的流化床催化剂

本发明涉及丙烯氨氧化生产丙烯腈的流化床催化剂，特别是关于催化剂的载体二氧化硅。

丙烯腈是重要的有机化工原料，它是通过丙烯氨氧化反应生产的。为获得高活性、高选择性的流化床催化剂，人们经过不断探索，作出了一系列改进。这些改进大都涉及催化剂的活性组份，很少涉及催化剂的载体。在丙烯氨氧化制丙烯腈的过程中，催化剂的载体一般可用二氧化硅、硅藻土、浮石、石英砂等，而最常用的是二氧化硅。催化剂中的二氧化硅可来自硅溶胶、硅凝胶，已成型的微球硅胶、正硅酸乙酯等，最好为硅溶胶。

虽然载体二氧化硅对丙烯氨氧化生产丙烯腈没有催化活性，但对上述活性组份在催化剂中的分散状态、催化剂的孔结构和物理性质有重要影响，对于流化床丙烯腈催化剂来说，某些物理性质如耐磨强度、堆积密度等十分重要。

有关载体二氧化硅的改进文献报道不多，已发表的专利多数是针对以氧化铈为基本成份的铈系催化剂。例如，特公昭57-26592提出，对铈铁系催化剂要求硅溶胶的胶粒平均粒径为5~100毫微米，二氧化硅浓度为10~60%，特公平2-47264提出，在制造铈系催化剂时，用两种不同胶粒粒径的硅溶胶，制成催化剂有较好的耐磨强度，A种硅溶胶的粒径为 $5 < D_a < 50$ 毫微米，B种胶粒为 $0.1 < D_a/D_b < 0.9$ 。对钼系催化剂而言，二氧化硅的改进文献更少，特公平3-16177提出了制造铈酸盐催化剂时，载体二氧化硅用两种成分：一种是用四氯化硅在高温下焙烧制成的微粒二氧化硅，另一种是硅溶胶，同时也将这种方法

应用于制造钼系催化剂 (US 4280929)，以提高耐磨强度。上述文献中，使用硅溶胶的方法操作繁琐，控制困难，需二次以上添加硅胶。为获得一种催化剂制备更方便，同时制成的催化剂具有更好的强度与活性，使之更适合丙烯氨氧化生产丙烯腈的流化床的要求，我们发明了一种最佳的催化剂。

本发明的构思是通过以下的技术方案实现的。用于本发明的流化床催化剂是由二氧化硅载体和具有如下化学式组成的组合物组成的：



式中A为钾、铷、铯、钐、铈或它们的混合物；B为锰、镁、锶、钙、钡、镧、稀土元素或它们的混合物；C为磷、砷、硼、锑、铬或它们的混合物；M为钨、钼或它们的混合物。

a为0.01~1，最佳为0.03~0.4；b为0.1~3，最佳为0.5~2；c为0.01~2，最佳为0.1~1.5；d为0.01~8，最佳为0.5~5；e为0.01~12，最佳为0.5~8；f为0.2~0.7，最佳为0.3~0.5；g为0.01~8，最佳为0.1~4；h为0.01~6，最佳为0.1~4；i为0.01~6，最佳为0.1~3；j为6~11.99，式中i与j的总和恒为12；x为满足催化剂中各元素化合价所需氧原子数的总和。

催化剂中载体二氧化硅含量为30~70% (重量)，最佳为40~60% (重量)。

本发明人在中国专利1033014A (CN 1005248B)，1022439A (CN 1013079B)，1061163A (US 5177048)，1054914A (CN 1021638B，US 5223469，EP 484792A) 和1061166A分别发表了有关上述催化剂的化学组成，制造方法和工业应用等方面的改进结果，本专利是上述催化剂有关载体二氧化硅的新结果。

本发明催化剂中各组份所使用的原料为：

组份A类元素最好用硝酸盐、氢氧化物或可分解为氧化物的盐类；

组份B类元素可用氧化物或可分解为氧化物的盐类；

组份C类元素中的磷、砷和硼最好用相应的酸类或其铵盐，铬最好用三氧化铬(六价铬)，硝酸铬或两者的混合物，铈可用三氧化二铈，五氧化二铈，水解可生成氧化物的卤化物及铈溶胶。

组份钠可用硝酸钠、氢氧化钠、硅酸钠或可以分解的钠化合物，钠的加入量应扣除硅溶胶中含钠量。

组份镍、钴、铁、铋可用氧化物或可以分解为氧化物的盐类，所用的盐类最好是水溶性的硝酸盐。

组份M类元素中的钨可用氧化钨或钨酸铵，钒用偏钒酸铵。

组份钼可用氧化钼或钼酸铵。

为保证催化剂具有较高的活性和良好的耐磨强度，对上述通式的钼系催化剂，作为载体二氧化硅的原料需使用一种特殊规定的硅溶胶。该硅溶胶的平均粒径过小则制成的催化剂孔径小，氨氧化时碳的氧化物生成量大，选择性低。另外，粒径太小将使制造催化剂的喷雾浆料粘度过大和不稳定，容易发生凝胶。粒径过大则制成的催化剂耐磨强度不好，本专利要求胶粒的平均粒径为10~200毫微米，最好为15~90毫微米，硅溶胶中二氧化硅浓度为5~60(重量)，最好为30~40%(重量)，二氧化硅浓度过低则制成的催化剂堆积密度小，消耗大。硅溶胶的PH值与催化剂的化学组成有关，在本专利上述的化学通式前提下，PH值为7~12，最好为9~11。硅胶中钠的含量为100~2500ppm，最好为500~1500ppm。

用该溶胶与催化剂各组份和水混合成浆料，经喷雾干燥成型为微球状，最后焙烧制成催化剂。浆料的配制是将催化剂各组份的水溶液和载体硅溶胶按中国专利CN 1005248 B所述的方法进行。

用上述方法制得的催化剂，在流化床反应器上进行催化剂的活性、选择性与耐磨强度评价，效果良好，取得了预期的效果。

以下是本发明催化剂的实施例，其中丙烯转化率、丙烯腈选择性和单程收率的定义如下：

$$\text{丙烯转化率 (\%)} = \frac{\text{反应的丙烯摩尔数}}{\text{丙烯进料摩尔数}} \times 100$$

$$\text{丙烯腈选择性 (\%)} = \frac{\text{生成丙烯腈摩尔数}}{\text{反应的丙烯摩尔数}} \times 100$$

$$\text{丙烯腈单程收率 (\%)} = \frac{\text{生成丙烯腈摩尔数}}{\text{丙烯进料摩尔数}} \times 100$$

#### 实施例1

将9.2克重量浓度为20%的硝酸钾溶液、13.4克重量浓度为20%的硝酸铷溶液和8.9克重量浓度为20%的硝酸铯溶液混合为物料(A)。

将23.7克钨酸铵溶于100毫升重量浓度为5%的氨水，再与368.3克钼酸铵与300毫升50~95℃热水组成的溶液相混合得物料(B)。

将79.2克硝酸铋、52.1克硝酸锰、131.9克硝酸铁、211.1克硝酸钴、121.3克硝酸镍和29.0克硝酸铬混合，加水70毫升，加热溶解得物料(C)。

所用硅溶胶的平均粒径为25毫微米，钠含量(以氧化钠计)为1350 ppm，PH值为9。

将物料(A)与1250克重量浓度为40%的上述硅溶胶混合，搅拌下加入5.23克重量浓度为85%的磷酸和物料(B)和(C)，充分搅拌得浆料，按常法将制成的浆料在喷雾干燥器中成型为微球状，最后在内径为89毫米、长度为1700毫米的焙烧炉中于700℃焙烧1小时。

制成的催化剂比表面积为25米<sup>2</sup>/克，堆积密度为0.98克/毫升，

耐磨强度为2.7% (按Test Methods for Synthetic Cracking Catalysts法测定)。

制成的催化剂放入内径为38毫米的流化床反应器内, 在反应温度435°C、反应压力为0.08兆帕、丙烯:氨:空气=1:1.2:10.0(摩尔), WHH为0.045的条件下进行活性评价, 结果如下:

丙烯转化率:	97.5%
丙烯腈单收:	81.0%
丙烯腈选择性:	83.1%

### 实施例2

原料加入量与实施例1相同, 所用载体硅溶胶的规格, 除钠含量为900ppm以外, 其余均相同, 按实施例1方法制成催化剂, 其比表面积为16米<sup>2</sup>/克, 耐磨强度为4.0%。活性评价条件与实施例1相同, 结果如下:

丙烯转化率:	98.3%
丙烯腈单收:	81.5%
丙烯腈选择性:	82.9%

### 实施例3

原料加入量与实施例1相同, 所用载体硅溶胶的规格, 除钠含量为500ppm以外, 其余均相同, 按实施例1方法制成催化剂, 其比表面积为19米<sup>2</sup>/克, 耐磨强度为6.5%。活性评价结果如下:

丙烯转化率:	99.4%
丙烯腈单收:	81.6%
丙烯腈选择性:	82.1%

由本例可知, 硅溶胶中的钠含量过低, 则催化剂耐磨强度差, 催

化剂的活性虽然较高，但丙烯腈选择性下降。

#### 实施例4

按实施例1所述方法制造催化剂，物料(A)用重量浓度均为20% 的9.0克硝酸铯溶液，41.0克硝酸钐溶液和24.6克硝酸亚铈溶液混合制成。

物料(B)是用24.1克钨酸铵溶于100毫升重量浓度为5%的氨水溶液，再和374.1克钼酸铵与300毫升50~95℃热水组成的溶液相混合制成。

再用80.4克硝酸铋，134.0克硝酸铁，52.9克硝酸锰，94.5克硝酸镁，107.2克硝酸钴，123.2克硝酸镍，29.5克硝酸铬与70毫升水配制成物料(C)。

载体硅溶胶中钠含量为1000ppm，胶粒平均粒径为30毫微米，二氧化硅含量为40%(重量)，PH为9.5。

将上述物料(A)，(B)，(C)和1250克硅溶胶及5.3克重量浓度为85%的磷酸混合，喷雾成型，焙烧，制成催化剂。

制成的催化剂比表面积为16米<sup>2</sup>/克，堆积密度为1.02克/毫升，耐磨强度为3.0%。活性评价方法和条件与例1相同，结果如下：

丙烯转化率： 97.5%

丙烯腈单收： 79.5%

丙烯腈选择性： 81.5%

#### 实施例5

按实施例1所述方法制造催化剂，物料(A)用重量浓度均为20% 的11.0克硝酸钠，17.5克硝酸钾，8.5克硝酸铯溶液混合制成。

物料(B)是用4.1克偏钒酸铵和361.0克钼酸铵与300毫升50~95℃热水混合制成。

84.1克硝酸铋, 140.0克硝酸铁, 75.2克硝酸亚铈, 242.0克硝酸钴, 74.6克硝酸锰, 18.7克硝酸铬, 11.5克硝酸铈与100毫升水混合配成物料(C)。

载体硅溶胶中钠含量为700 ppm, 平均粒径为20毫微米, 重量浓度40%, PH 9.0。

将上述各物料(A), (B), (C)与1250克硅溶胶和16.1克硼酸混合, 喷雾成型, 再于600℃焙烧0.5小时制成催化剂。

制成催化剂比表面积为20米<sup>2</sup>/克, 堆积密度为0.98克/毫升, 耐磨强度为3.0%, 按实施例1进行催化剂活性评价, 结果如下:

丙烯转化率:	98.0%
丙烯腈单收:	81.3%
丙烯腈选择性:	82.9%

#### 实施例6

按实施例5方法制造催化剂, 各组分加入量均不变, 硅溶胶的平均粒径为5毫微米、浓度为25%(重量)、PH值为8, 其余规格与实施例5相同。按实施例5方法制造催化剂时, 发现浆料粘度较高, 喷雾干燥比较困难, 催化剂损失较大。

制成的催化剂比表面积为21米<sup>2</sup>/克, 堆积密度为0.85克/毫升, 耐磨强度为3.8%。按实施例1进行评价, 结果如下:

丙烯转化率:	98.0%
丙烯腈单收:	80.6%
丙烯腈选择性:	82.2%

从本实例可知, 硅溶胶的胶粒过小, 主要影响催化剂的物理性质, 对催化活性影响不大, 催化剂堆积密度过小将影响流化床反应器的正常操作, 也给催化剂的制造造成困难。

### 实施例7

按实施例5方法制造催化剂，各组分加入量均不变，硅溶胶的平均粒径为200毫微米，其余规格与实施例5相同。

制成的催化剂比表面积为23米<sup>2</sup>/克，耐磨强度7.0%，按实施例1进行催化剂活性评价，结果如下：

丙烯转化率：98.3%

丙烯腈单收：79.8%

丙烯腈选择性：81.2%

由本实例可知，硅溶胶的胶粒过大，则催化剂的耐磨性不好，不适用于流化床反应器。

### 实施例8

按实施例4方法制造催化剂，各组分加入量均与实施例4相同，硅溶胶的平均粒径为80毫微米，其余规格与实施例4相同。

制成的催化剂比表面积为28米<sup>2</sup>/克，按实施例1条件进行活性评价，结果如下：

丙烯转化率：99.0%

丙烯腈单收：76.4%

丙烯腈选择性：77.2%

由本实施例可见，虽然硅溶胶粒径在规定范围以内，但表面积过大则丙烯腈选择性降低，反应中生成较多二氧化碳。

将本实施例催化剂的焙烧温度提高到750℃，焙烧时间改为45分钟，制成的催化剂比表面积为22米<sup>2</sup>/克，按实施例1条件进行活性评价，结果如下：

丙烯转化率：97.6%

丙烯腈单收：80.5%

丙烯腈选择性: 82.5%

本实施例说明, 硅溶胶的粒径在规定范围内, 但粒径不同, 也需调节焙烧条件取得最佳结果。